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Applications of Titanium Dioxide Materials

Xiaoping Wu

Abstract

Titanium dioxide (TiO_2) is a stable, non-toxic inorganic material. Because of very high refractive index, TiO_2 has been widely used as a white pigment. The optimal particle sizes of TiO_2 for pigment applications are around 250 nm. The pigmentary applications of TiO_2 can be found in many common products such as paints, plastics, paper and ink. Global titanium dioxide pigment sales have reached several million tons annually. Titanium dioxide is also a semiconducting material. When excited by photons which have energy equal to or higher than the band gap of TiO_2 , electron/hole pairs can be generated. The dynamics of the photo-generated electron/hole pairs of TiO_2 is fundamentally important to its photocatalytic properties. More recently, nano-structured TiO_2 has raised a great deal of interests in research after the discoveries of the important potentials for applications. The enormous efforts have been put in the preparation, characterization, scientific understandings, and modifications of the photocatalytic properties of TiO_2 . The applications of nano-structured TiO_2 can be now found in a wide range of areas including electronic materials, energy, environment, health & medicine, catalysts, etc. This chapter has discussed and highlighted the development of the applications of titanium dioxide materials in many of those areas.

Keywords: Titanium dioxide, Applications, Pigment, Nano-structured

1. Introduction

Titanium dioxide (TiO_2) is an inorganic substance that is used extensively as a white pigment. Compared with many other inorganic pigments, TiO_2 has the advantages of high stability, being non-toxic, and low cost. TiO_2 have three polymorphs: anatase, rutile and brookite, but only anatase and rutile crystal forms have been useful as pigment. Both anatase and rutile crystals have very high refractive indices, and their particles can scatter visible light almost completely [1]. The optimum particle size of TiO_2 for pigment applications is around 250 nm. In the early application of TiO_2 as pigment, it was found that paint faded more rapidly than others when painted films were exposed to the Sun and ultraviolet (UV) light. Coating with inorganic compounds such as alumina or silica suppressed the catalytic activity on the surface and improve the weather resistance, leading titanium dioxide in wide applications as white pigment. Global titanium dioxide pigment sales were about 6 million tons in 2017 and the growth trend of global titanium dioxide pigment sales is continuing over the recent years [2].

In the 60s of the last century, scientists studied the photo-induced phenomena on the solids of TiO_2 and ZnO under UV light irradiation [3–5]. In the early 1970s, research on photocatalysis by TiO_2 got wide attention due to the historic discovery of the electrochemical water splitting by use of TiO_2 [6]. In the 1990s, photocatalytic research of TiO_2 had made progress in the practical applications of TiO_2 in the decomposition of harmful organic materials [7, 8]. A function of super hydrophilicity of TiO_2 was also discovered [9]. Since the beginning of this century, nano-structured TiO_2 has attracted extensive interests. When the particle sizes of TiO_2 are reduced down to the nano-meter scale (generally in 1–100 nm), the surface characteristics and surface areas of TiO_2 have changed dramatically. The new or enhanced physical and chemical properties of nano-structured TiO_2 begin to emerge. The photocatalytic property of nano-structured TiO_2 has been greatly enhanced because of the changes in the surface characteristics and surface areas. Quantum effects of nano-structured TiO_2 can also have a role to play, affecting its photocatalytic, optical or electronic properties. As the results of academic and industrial research in recent years, enormous progresses have been made in the preparation, characterization, and scientific understandings of nano-structured TiO_2 . Nano-structured TiO_2 have begun to find applications in a wide range of areas including electronic materials, energy, environment, health & medicine, sensors, catalysts, etc.

TiO_2 pigment is industrially produced from titanium containing ores by using a Chloride or Sulfate process [1, 10]. Nano-structured TiO_2 are made in the different ways, depending on the material characteristics required for the specific applications. A number of innovative fabrication methods of nano-structured TiO_2 materials have been developed and are used for different applications. These methods can be broadly classified as the liquid phase or the gas phase methods. Nano-particles, nano-wires, nano-tubes, two or three-dimensional nano-structured TiO_2 materials can also be fabricated for different applications [11–18].

This chapter will discuss and highlight the recent development of applications of titanium dioxide as pigment and as functional materials in the areas of energy, environment, catalyst, and biomedicine.

2. Application of titanium dioxide as pigment

2.1 Light scattering of pigmentary TiO_2

The main use of titanium dioxide is white pigment, because it absorbs almost no incident light in the visible region of the spectrum (380–700 nm). Titanium dioxide has a strong light scattering power, and scatters incident light in three ways: surface reflection, refraction and diffraction in the crystal [1]. When the refractive index difference between titanium dioxide and medium increases, the reflected light increases and complies with Eq. (1):

$$R = \frac{(n_p - n_m)^2}{(n_p + n_m)^2} \quad (1)$$

n_p and n_m are the refractive index of pigment and medium, respectively [1]. Titanium dioxide has a high refractive index (refractive index of rutile and anatase titanium dioxide is 2.70 and 2.55 respectively) [19]. These high refractive index values enable the rutile and anatase TiO_2 pigments to have much greater hiding power in coatings or in plastics, making TiO_2 to be a much better pigment than the

other chemical substances. Therefore, under the same conditions, only less titanium dioxide is needed to form a coating, which is white and opaque. Studies have shown that the optical properties of titanium dioxide pigments are related to their particle size, and the optimum of particle size of pigmentary titanium dioxide is around 250 nm [1].

2.2 Application areas

Pigmentary TiO_2 is inert, non-toxic, stable and less costly. Over 50 percent of all TiO_2 pigment produced is consumed by the coatings industry, and approximately a quarter by the paper industry. Eleven per cent goes into plastics; remaining a few percent into inks and other end-uses [20]. Titanium dioxide particles optimized with particle size and surface treatments have excellent hiding power, brightness, and other important features such as resistance to chemical degradation. Rutile pigment is more resistant to UV light than anatase, and is preferred for paints, plastics, especially for the applications in outdoor conditions. Anatase pigment is less abrasive and is used mainly in indoor paints and in paper manufacture. TiO_2 is surface treated with one or more inorganic oxides such as alumina, silica, zirconia or a combination of these inorganic oxides, and organic compounds such as polyhydric alcohol to have the required properties of dispersion, photoactivity, and opacity required for a specific application [21].

In coating applications, a relatively high quantity of TiO_2 pigment must be used to achieve desirable hiding effect on the coating substrates, because coatings of titanium dioxide are usually in the form of very thin layers. The pigment volume concentration (PVC) is practically used to specify the amount of TiO_2 in a coating. Different types of paints containing TiO_2 pigment will have different levels of PVC, depending on different coating applications. TiO_2 coatings are used to cover a wide range of surfaces, including indoor and outdoor building, wood products, metal objects, domestic and industrial equipment [21].

In plastics applications, titanium dioxide pigment is used to opacify plastic materials. In some applications, TiO_2 is used to improve photodurability. The requirements for TiO_2 in plastics are good dispersibility in a polymer system and good heat stability. Hydrophobic organic surface treatments on the pigments are utilized to facilitate their dispersion in the viscous molten plastic resin. These are often silicone oils and other organic compounds for specialized uses. In many plastics applications, a blue undertone is also desirable to mask an intrinsic yellowness in the color of the resin or a slight degradation that occurs during the high-temperature processing. For this reason, plastics pigments often have a smaller crystal size than those for coatings applications [19].

The amount of titanium dioxide used in paper industry is the third largest after coating and plastic industries [20]. Although other white pigments can be used in paper industry, the production of high quality papers must use titanium dioxide as pigment. Titanium dioxide imparts desirable brightness and opacity to high-quality papers. Papers containing titanium dioxide pigment have high strength and have appearance to be white, shiny, thin and smooth. Because photochemical stability is not as critical in paper as in paint, both anatase and rutile pigments are widely used in paper industry.

In inks applications, performance requirements for TiO_2 pigment are different from coatings, plastics and paper. Inks are usually applied to produce a much thinner film on a surface than a general coating. It is very important to choose titanium dioxide particles with good shape, suitable size and size-distribution, smooth surface and non-angular. The type of TiO_2 can also affect the rheology, abrasiveness, gloss and redispersibility for ink products and applications.

TiO₂ is also widely used as a pigment for coloring of different products in pharmaceuticals and cosmetics industries. The characteristics of titanium dioxide provide interesting colors and allow new properties to pharmaceuticals with very small amounts of pigments. There are many products in this field that contain titanium dioxide, including: shampoos, creams, sunscreens, toothpaste, etc. [10].

3. Applications TiO₂ in energy generation and storage

With the special physical and chemical properties, nano-structured titanium dioxide has shown a number of promising application prospects in energy generation and storage. These include: solar cells, hydrogen production, and lithium battery [22–24].

3.1 Application of TiO₂ in dye-sensitized solar cell (DSSC)

The solar energy is a clean, abundant and renewable energy [25]. The current technology for the conversion of sunlight to electrical power is predominately silicon-based solid state solar cells. In recent years, the new semiconducting material-based solar cells have emerged to offer the possible alternative photovoltaic technology with prospect of cheap fabrication and flexibility [26–28]. Nano-structured TiO₂ has been the main semiconducting material for this new generation of solar cells. In this technology, an electron sensitizer absorbing in the visible is used to inject charge carriers across the semiconductor-electrolyte junction into TiO₂ to enhance the conversion efficiency from solar energy, because TiO₂ with its band gap of 3.2 electronvolt (eV) absorbs only the ultraviolet part of the solar energy. This type of solar cells is therefore called dye-sensitized solar cells (DSSCs). The dye-sensitized solar cells (DSSCs) have exhibited high performance and have the potential to be low-cost [29–33].

Figure 1 illustrates the working principle of a dye-sensitized solar cell. The dye-sensitized solar cell consists of two electrodes, a dye-sensitized nano-structured TiO₂ mesoporous layer, and a liquid electrolyte containing redox system (I[−]/I₃[−]). The nano-structured TiO₂ mesoporous layer with a monolayer of the charge transfer dye at its surface is placed in contact with a redox electrolyte. Under solar

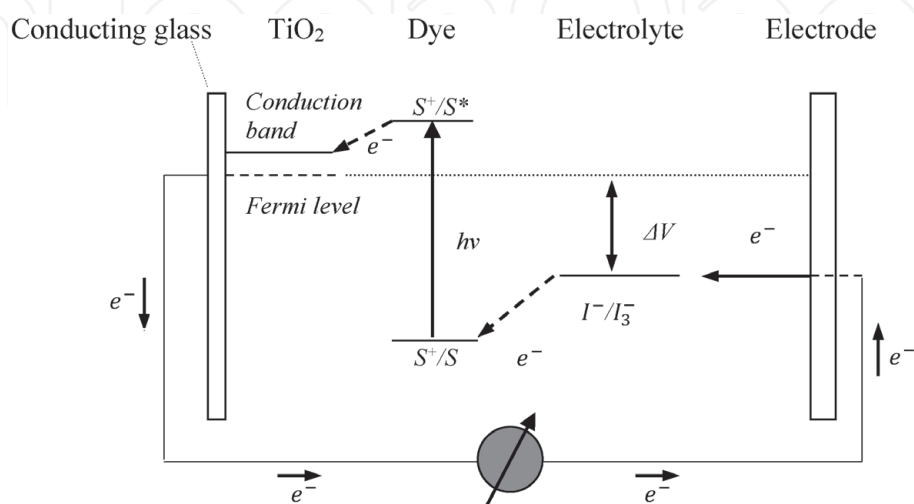


Figure 1. Working principle of a dye-sensitized solar cell. S, S⁺, and S* represent dye sensitizer, oxidized dye sensitizer, and excited dye sensitizer, respectively. ΔV is the difference between Fermi level and electrochemical potential of the electrolyte.

irradiation, the charge transfer dye injects electrons into the conduction band of TiO_2 , and the electrons are conducted to the external circuit to produce electric power. The original state of the dye is subsequently restored by an electron donation from the electrolyte (for example, an organic solvent containing a redox system of iodide/triiodide couple).

The nano-structured TiO_2 mesoporous layer in a dye-sensitized solar cell has a much larger surface area available for the dye-chemisorptions. The kinetic processes occurring in a dye-sensitized solar cell have been profoundly changed as a result of using nano-structured TiO_2 . Solar energy-to-electricity conversion efficiencies of DSSCs have been increased. The record for the highest certified single cell and DSSCs module efficiencies are 11.9% and 8.8%, respectively [34].

More recently, TiO_2 is used in a new type of solar device so-called pervoskite solar cells. As in DSSCs, TiO_2 is used as a mesoporous layer. However, instead of using organic dye in DSSCs, organic lead complex (for example, $\text{CH}_3\text{NH}_2\text{PbI}_3$) is used to inject electrons into the conduction band of TiO_2 . In a short period of the recent few years, the reported efficiency of pervoskite solar cells was 9.7% initially, and then 12.0% [35, 36]. Further progress was made with efficiencies above 15.0% [37]. The record for the highest certified single cell and minimodule efficiencies are 20.9% and 16.0%, respectively [34].

3.2 Application of TiO_2 in hydrogen production

In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode under UV light [6, 38, 39]. Compared with other photocatalysts, TiO_2 is much more promising as it is stable, non-corrosive, environmentally friendly, abundant and cost effective. **Figure 2** illustrates the mechanism of the photocatalytic hydrogen production by TiO_2 semiconducting materials. When excited by photons which have energy equal to or higher than their band gap (E_g), electrons (e^-) in valence band (VB) of TiO_2 are promoted from to the conduction band (CB). Simultaneously, Holes (h^+) create in VB of TiO_2 . The process of generating (e^-) and (h^+) in TiO_2 with excitation by photons is described with Eq. (2):



The photo-generated (e^-) and (h^+) in TiO_2 can recombine, releasing energy in the form of heat or photons. The photo-generated (e^-) and (h^+) that migrate to the surface of TiO_2 without recombination can reduce and oxidize H_2O molecules adsorbed on the surface of TiO_2 to generate H_2 and O_2 .

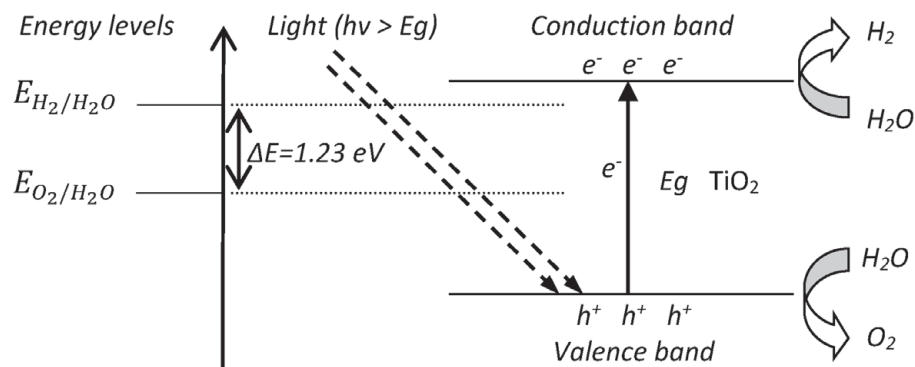


Figure 2.
Illustration of mechanism of photocatalytic hydrogen production by TiO_2 .

As can be seen in **Figure 2**, the conduction band level of TiO_2 is more negative than the hydrogen production level ($E_{\text{H}_2}/\text{H}_2\text{O}$), and the valence band is more positive than water oxidation level ($E_{\text{O}_2}/\text{H}_2\text{O}$). ΔE , representing the energy difference between hydrogen production level and water oxidation level, is 1.23 eV. The conduction and valence band levels of TiO_2 meet the requirement for hydrogen production. As in dye-sensitized solar cell, nano-structured TiO_2 can enhance the photocatalytic reactions for the generation of hydrogen by a number of ways. For example, much more surface area per mass is available for adsorption of water due to the decreased particle sizes of TiO_2 nano-particles. The surface of TiO_2 nano-particles can also become more reactive because much higher portion of atoms exists at the surface. Furthermore, the quantum effect of TiO_2 nano-particles becomes more significant as particle size of TiO_2 is getting very small. Nano-structured TiO_2 has been known to be stable, chemically inert, and low cost.

Despite many advantages of using TiO_2 for photocatalytic hydrogen production, the efficiency using solar energy for water-splitting by TiO_2 is still low, and is currently not been used for industrial scale of hydrogen production. The low energy conversion efficiency of TiO_2 in water-splitting is believed to be caused by the wasteful recombination of electron/hole pairs, backward reaction of combining hydrogen and oxygen into water, and limitations for TiO_2 to utilize visible light due to its large band gap. Research has been carried out to produce nano-structured TiO_2 with a narrower band gap in order to utilize visible-light energy more efficiently. Progresses have been made in modifying the band gap of nano-structured TiO_2 by means of metal loading, ion doping, metal ion-implantation, dye sensitization and composite TiO_2 . Noble metals, such as Pt, Au, Pd, and Ag, have been reported to be very effective in enhancing TiO_2 photocatalysis [40–43]. Carbon-doped nano-structured TiO_2 have showed much more efficient water splitting under visible-light illumination [44]. A study using a dye sensitizer for photocatalytic hydrogen production was investigated [45]. A visible light absorber, C_3N_4 , has been coupled to many wide-band gap semiconductors to improve solar harvesting. A 50 wt % $\text{C}_3\text{N}_4/\text{TiO}_2$ junction was found to double H_2 evolution compared to pure C_3N_4 under visible irradiation [46].

3.3 Application of TiO_2 in energy storage

Lithium-ion batteries are a type of rechargeable batteries commonly used in consumer electronics. Lithium ion battery system and technology has been a revolutionary change in the field of power supply battery. Anode materials based on titanium oxides are the promising candidates as alternative materials to carbonaceous anodes due to advantages in terms of cost, safety and toxicity [47, 48]. TiO_2 also exhibits excellent structural stability, high discharge voltage plateau (more than 1.7 V versus Li^+/Li), and excellent cycling stability [49, 50].

Typically the Li^+ insertion–extraction reaction for TiO_2 polymorphs occurs according to reaction (3):



x can range between 0 and 1, depending strongly on the polymorph, particle size, and morphology of TiO_2 . The maximum theoretical capacity is 335 mAh g^{-1} which corresponds to $x = 1$. This makes TiO_2 a highly competitive alternative to graphite anodes having a theoretical capacity of 372 mAh g^{-1} [51–53]. However, TiO_2 has limitations, such as low capacity, low electrical conductivity, and poor rate capability. Strategies have been developed to address the issues of TiO_2 -based

anodes. These include the use of multi-dimensional nanostructured TiO_2 , composite and coating materials, and element doping.

One dimensional anatase TiO_2 nanofiber anodes were used as an anode active material in Li ion batteries and exhibited a high lithium storage capacity, a stable cycle life, and good rate capability [54]. Two dimensional TiO_2 nanosheets have been shown to exhibit the superior capacities, improved cycling stability and rate capabilities, owing to unique exposed facets, shortened path, and reserved porous structures [55–57]. Nanostructured TiO_2 is a low voltage insertion host for Li and a fast Li insertion/extraction host [58, 59]. These characteristics provide nanostructured TiO_2 a potential anode material for high-power Li-ion batteries. Studies on the use of nanostructured TiO_2 as anode with LiCoO_2 cathode demonstrated specific capacity of 169 mAh g^{-1} [60]. Xu, et al. investigated electrochemical performance of TiO_2 -coated LiCoO_2 and LiMn_2O_4 in different potential regions [61]. Mechanically blended composite of nanosized TiO_2 and carbon nanotubes (CNTs) has been used as potential anode materials for Li-ion batteries. It was found that the TiO_2 /CNTs nanocomposites exhibited an improved cycling stability and higher reversible capacity than CNTs [62, 63]. Metal oxide coatings containing TiO_2 can efficiently improve the capacitive performance of the materials through synergistic effects in an electrode system [64–67].

4. Application of TiO_2 in environment protection

4.1 Fundamental

Excitation of TiO_2 with UV light with energy greater than the band gap ($>3.2 \text{ eV}$) promotes electrons from valence band into the conduction band and generates electron/hole pairs [68, 69]. **Figure 3** illustrates the mechanism of generating reactive radicals from TiO_2 under irradiation of UV light. The conduction band electrons e^- can reduce molecular oxygen to generate ($\text{O}_2^{\bullet-}$) superoxide radicals, and valance band holes h^+ is positive enough to generate (OH^{\bullet}) radicals from H_2O or OH^- on TiO_2 surface. OH^{\bullet} radicals have the strongest oxidation potential. Superoxide radicals ($\text{O}_2^{\bullet-}$) have moderate oxidation potentials, but their diffusion distances can reach up to hundreds of micrometers [70]. Both radicals are very reactive, and they attack the organic matter present or near the surface of TiO_2 to degrade toxic and bio-resistant compounds or species into CO_2 , H_2O , etc. [69, 71].

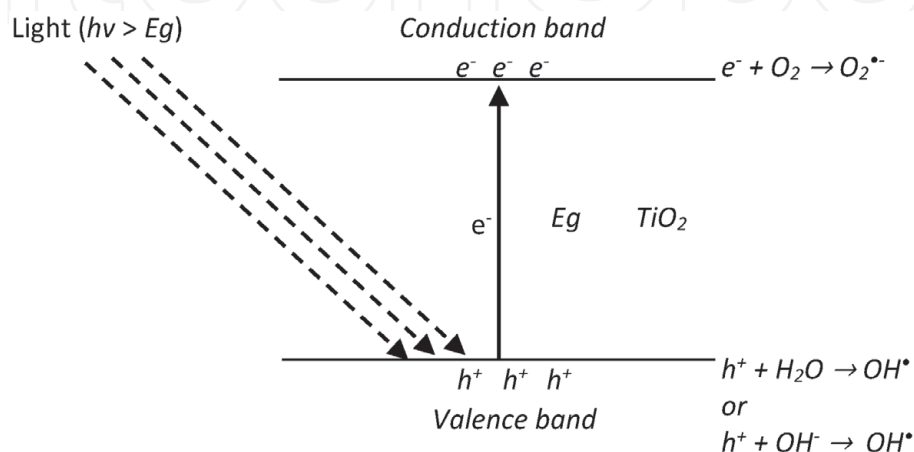


Figure 3.
 Mechanism of generating reactive radicals (OH^{\bullet}) and superoxide ($\text{O}_2^{\bullet-}$) from TiO_2 under irradiation of UV light.

The generation of reactive radicals (OH^\bullet) and ($\text{O}_2^{\bullet-}$) is affected by the crystalline state, and properties such as surface area and particle size. Although anatase and rutile have the similar band gaps, anatase has shown to have more rapid rate in photo-degradation of organic or bio-resistant compound than rutile [72, 73]. Therefore, nano-structured anatase TiO_2 is often used as a catalyst in photo-degradation applications.

4.2 Self-clean and antibacterial uses of TiO_2

One application, which is commercially successful, is the nano-structured TiO_2 material for self-clean and antibacterial uses [68, 74, 75]. Many nano-structured TiO_2 material based products have been used as construction materials [76–82]. Self-clean application is based on the actions of sunlight, rainwater, and photocatalytic properties of TiO_2 . Under the irradiation of sunlight, adsorbed organic materials like oil can be decomposed by hydroxyl radicals on the surface of TiO_2 . Because of the hydrophilic property of TiO_2 surface, contaminants and dust can be washed away off by rainwater. Tiles containing nano-structured TiO_2 have been used to construct photocatalytic surface to decompose bacteria and viruses on the surface or bacteria floating in the air as they come in contact with surface.

Studies have shown that the photocatalytic properties of TiO_2 can sometimes be enhanced by doping TiO_2 with different elements. For example, TiO_2 nano-particles containing Ag^+ have been widely used in antibacterial plastics and coatings [83–85]. Fe or Sb-doped TiO_2 have been used to make coatings with high antibacterial property [79, 80].

Nano-structured self-clean glass is now an important commercial product. Pilkington Glass has developed the first self-cleaning windows. The window glass is coated with a very thin and transparent TiO_2 layer to have the properties of photocatalysis and hydrophilicity on the glass surface. Photocatalysis of TiO_2 break down the organic dirt adsorbed onto the window in sunlight, and the decomposed organic species is washed away efficiently by rain or other water in the form of thin layer instead of droplets [86].

4.3 Application of TiO_2 in water-treatment

Another important application of nano-structured TiO_2 is in the water-treatment, utilizing its photocatalytic properties [87–92]. Research of using nano-structured TiO_2 for water-treatment has been very active in recent years. TiO_2 has been used in the photocatalytic decomposition of organic dyes in waste water, and organic pollutants such as pesticides, dyes and pharmaceuticals in other contaminated water [93, 94]. The photocatalytic decomposition of organic matters in water are all based on the mechanism of the generation of highly reactive radicals (OH^\bullet) and superoxide ions ($\text{O}_2^{\bullet-}$) in TiO_2 under UV irradiation, as illustrated in **Figure 3**. TiO_2 has been considered to be the best choice to be used as photo-catalysts, as TiO_2 is chemically inert, and cheap to manufacture and to apply.

The complete separation and recycling of TiO_2 fine particles is important for the practical applications. A number of innovative methods have been developed for this purpose. For example, fixing TiO_2 nano-particles on supports such as glass plates, aluminum sheets, and activated carbon are investigated to recycle the catalyst [95], or developing TiO_2 catalyst system which can be separated from reaction liquid by applying external magnetic field [96, 97].

Because TiO_2 and many other semiconductors have the large band gaps, the application of photocatalytic water treatment using TiO_2 is limited by its relatively low efficiency. To improve photocatalytic efficiency of TiO_2 for water treatment, as

well as other photocatalytic applications, Enormous research has been carried out to extend the photocatalytic response of TiO_2 into the visible range [98]. One of the strategies for improving photocatalytic efficiency for water treatment is to modify the band gap of TiO_2 by incorporation of other ions into TiO_2 structure, through metal and non-metal doping, metal implantation, noble metal loading, and others [99–104].

5. Application of TiO_2 in catalyst

TiO_2 -based composite materials have been widely used as catalysts [105–107]. TiO_2 is used as support in commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts for the selective catalytic reduction (SCR) of NO_x . In SCR technology, highly undesirable NO_x acid gas emissions from various industrial sources are reduced to harmless N_2 and H_2O . The $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts are widely used in commercial applications because of their excellent thermal stability and lower oxidation activity for the conversion of SO_2 to SO_3 [108, 109]. The $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts have become the most widely used industrial catalysts for these SCR applications since the introduction of this technology in the early of 1970s [110].

TiO_2 has the potential to induce the reductive chemical transformation. The reductive photocatalysis of ethyne and ethene have been reported [111–113]. TiO_2 have been used as a useful catalyst for the reduction of carbonyl compounds such as aldehydes or ketones, nitro compounds, imines and for the some of the chemical transformations involving redox processes. Photocatalysis on TiO_2 is a light-driven redox reaction. Redox reactions can be induced by electrons (e^-) generated in conduction band (CB) and holes (h^+) simultaneously generated in valance band (VB) under the irradiation of light. The electrons in the conduction band are readily available for transferring while the holes in the valence band are open for donations [114]. The photocatalytic reduction of an electron acceptor can be carried out in the presence of a large excess amount of electron donors such as alcohols or amines, which are used to scavenge (h^+). Oxygen (O_2) is a competitive electron acceptor, and can influence the reduction reaction. Therefore, the reductive chemical transformation should be generally performed in an O_2 free environment. Under these conditions, a photocatalytic reduction proceeds through transferring electrons (e^-) in CB or trapped at surface defects of TiO_2 into the organic molecules adsorbed on TiO_2 surface. The photocatalytic reduction of aldehydes, nitro compounds, and imines have been reported. Aromatic aldehydes and ketones were reduced to the corresponding alcohols using TiO_2 as a photocatalyst [115, 116]. Aromatic and aliphatic nitro compounds were reduced to corresponding amines using TiO_2 as catalyst [117]. The direct reduction of imines to corresponding secondary amines was studied [118].

6. TiO_2 in health and biomedicine

6.1 TiO_2 in sunscreen

The sunlight reaching the earth's surface contains UV, visible and infrared wavelength. The Sun releases ultraviolet (UV) radiation in three different wavelengths, and all are harmful in different ways. These wavelengths in sunlight are called UVA (315–400 nm), UVB (280–315 nm) and UVC (100–280 nm) [119]. Because the earth's atmosphere blocks most UVC rays, UVC does not generally reach the earth's surface to a significant degree. Therefore, they are not thought to

be important contributors to the biological effects on human skin [120]. UVA wavelength penetrates more deeply into the skin causing photo-aging and the formation of skin cancer. UVB is shorter, and damages the surface of the skin. The damage from UVB can cause sunburn and cancer [121–124].

TiO₂ is a semiconducting material with very high refractive index. The high refractive index is what allows the substance to scatter visible light. The current method of preventive treatment against harmful UV radiation involves suspending a substance that either absorbs or scatters UV radiation in a thick emulsion, called sunscreen. Titanium dioxide (TiO₂) is an ingredient in sunscreens where its loading is frequently 2–15%. Sunscreen typically contains chemical filters that are organic compounds that absorb strongly the UV (most often UVB) and physical filters such as TiO₂ and ZnO that block UVA and UVB sunlight through absorption, reflection and scattering.

6.2 TiO₂ for cancer treatment

In biomedicine, TiO₂ nanoparticles with their extraordinary stability, exceptional photo-reactivity, and biocompatibility have a special place in biomedical solutions. The therapeutic potential of TiO₂ lies in the ability of these particles in response to light to produce reactive oxygen species (ROS). Production of ROS is the main factor in causing detrimental effects on cells. This effect was first applied by Cai *et al* in the immortal HeLa cell lines [125]. Distinct cell death was detected after HeLa cells were illuminated with UV light in the presence of TiO₂ (100 µg/mL). TiO₂ particles in the absence of light showed little cytotoxicity for concentration as high as 360 µg/mL. This demonstrated that the cells were killed by radicals produced from water upon illumination of TiO₂ particles and also oxidized by the photogenerated holes in TiO₂. Because the size and shape of TiO₂ nanoparticles have strongly influence in crystallinity, surface characteristics, electron/hole transportation and charge separation, it is important to be able to control the shape and size of TiO₂ nanoparticles to optimize their electronic and chemical properties, resulting in more efficient site-selective reactions. Various functionalized TiO₂ nanoparticles have been designed to be used in nanomedicine, as agents for photosensitization or sonosensitization and as drug carriers [126].

In both photodynamic therapy (PDT) and sonodynamic therapy (SDT), nanostructured titanium dioxide is used as an agent to produce reactive oxygen species (ROS). Photodynamic therapy (PDT) is an anti-tumor method in which photosensitive agent is applied and target area is illuminated for the activation of the agent. TiO₂ is normally a photocatalyst that produces oxidizing radicals by reacting with water during UV exposure and can damage nearby cells [127, 128]. Titanium dioxide and zinc oxide are two of the most effective photosensitizers for PDT applications. In sonodynamic therapy, TiO₂ acts as a sonocatalyst. Studies have shown that TiO₂ particles can promote the production of hydroxyl (OH[•]) radicals by ultrasound irradiation even in dark conditions [129, 130]. Ultrasound technology has been already used for some cancer therapies, either by generating localized heating using high intensity ultrasound or by activating a drug release using low intensity ultrasound. Ultrasound can penetrate inches below the skin. Therefore, it can be used to activate TiO₂ nanoparticles deep below the skin surface.

TiO₂ has been considered to be a good material for the design of drug carriers, for the reasons that the shape and size of TiO₂ nanoparticles can be engineered to control their electronic and chemical properties, and the surface of TiO₂ nanoparticles can be functionalized with various drug molecules [131, 132]. These capabilities bring new opportunities for more efficient site-selective chemistry of TiO₂, and form the vehicles for drug delivery applications.

7. Conclusions

Titanium dioxide is a stable, non-toxic inorganic material with very high refractive index, and can scatter visible light almost completely. The particle sizes for pigmentary TiO_2 are generally engineered to be around 250 nm to have optimized light scattering property. After coating with inorganic compounds such as alumina or silica, the catalytic activity on the surface of TiO_2 particles is suppressed and the weather resistance is improved. Because of the superior optical properties and chemical stability, TiO_2 has been developed and used as white pigment over several decades. Pigmentary titanium dioxide has excellent ability to impart brightness and opacity. Titanium dioxide has now been a well established inorganic white pigment and is widely applied in the coatings, plastics, paper manufacturing, and in many common products. Global sales of titanium dioxide pigment were about 6 million tons in 2017 and the growth trend of global titanium dioxide pigment sales is continuing over the recent years.

Titanium dioxide is also a semiconducting material which is characterized by a filled valence band and an empty conduction band. When excited by photons which have energy equal to or higher than their band gap, electrons (e^-) in valence band of TiO_2 are promoted to the conduction band and holes (h^+) are created in the valence band of TiO_2 . Because of the discovery of photocatalytic properties of titanium dioxide, and the ability to engineer TiO_2 nanomaterials for controlling their electronic and chemical properties, the applications of titanium dioxide as functional materials have become the focus of enormous research and development in the recent years. The applications of nano-structured TiO_2 can now be found in a wide range of areas including electronic materials, energy, environment, health & medicine, and catalysts. A number of materials containing nano-structured TiO_2 have become the important commercial products. Further research is continuing to modify the electronic and chemical properties, as well as surface characteristics of TiO_2 for the creation of more efficient TiO_2 functional materials in more specific application areas.

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Conflict of interest

The authors declare no conflict of interest.

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